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Sythesis of Cobalt Diamido Complexes via N-H Bond Activation

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Since the discovery of $CpCo(C_2H_4)_2$[1] in 1980, the Jonas reagent, $CpCo(C_2H_4)_2$ is attracting increasing attention in view of its unique chemical reactions. For example, Jonas reagent reacted with 3-hexyne or 2-hexyne to form a triple-decker complex[2] concomitant with extrusion of C_2H_4. Jonas reagent also reacted with a variety of alkynitriles[3] in the presence of alkyne, oximes,[4] and 1,2,3-triboracyclopentene[5] to give pyridine derivatives, nitrile complexes, and cobalt tripledecker complexes, respectively. In these reactions, the CpCo unit is presumed to be nucleophilic. Heck[6] reported cyclopentadienylcobalt diimine complex by the reaction of diiodocarbonylcyclopentadienylcobalt with phenylenediamine in the presence of base to remove 2 mol of hydrogen iodide. Transition metal diimine complexes have been reported, including derivatives of Co,[7] Rh,[8] Fe,[9] Cr,[10] Mo,[11] W,[12] Ru,[13] Ni, Pd, and Pt[14] by the reactions carried out under basic conditions, using KOH, NR_3 or an excess of the diamine in order to deprotonate the ligand. We[15] recently described the reaction of $[Cp^*MCl_2]_2$(M=Rh and Ir) and a variety of diamines in the presence of NEt_3 to give the rhodium and iridium diamido complexes. On view of the reactivity of CpCo unit, it occurred to us that the reaction of $CpCo(C_2H_4)_2$ and diamines led to N-H activation, forming the cobalt diamido complexes. Herein we reported the synthesis of cobalt diamido complexes by the reaction of $CpCo(C_2H_4)_2$ with a variety of diamines according to equation 1. The reaction of Jonas reagent with diamines in toluene gave a red solution, leading to N-H bond activation. The cyclopentadienylcobalt diamido complexes 1a-1c were isolated as relatively air-stable red crystals in 48-72% yield. It is interesting to note that Heck[6] and Murahashi[16] reported the same complexes 1a by the reaction of diiodocarbonylcyclopentadienylcobalt and o-phenylenediamine in the presence of NEt_3.

(1)

la X = H
lb X = Me
lc X = Cl
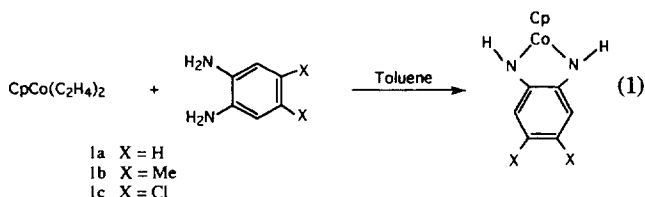
Maitlis and coworkers[8] also reported the complex $(C_5Me_5)Rh\{C_6H_4(NH)_2\text{-}1,2\}$ by the reaction of rhodium dimer with phenylenediamine. The structure of compounds 1a-1c were deduced from their ^{1}H NMR, IR and mass spectra. The compound 1a exhibits NH resonance at δ 8.96. The value is similar to that of authentic complex[6,16] appeared at δ 8.5-10. The value is also similar to that of $CymOs\{C_6H_4(NH)_2\text{-}1,2\}$[17] appeared at δ 8.68 and that of $Ni\{C_6H_4(NH)_2\text{-}1,2\}$ and $Cp^*Ir\{C_6H_4(NH)_2\text{-}1,2\}$ appeared at δ 8.80 and δ 8.23, respectively. A presumable product, $CpCo\{4,5\text{-}X_2\text{-}C_6H_2(NH_2)_2\text{-}1,2\}$ would be ruled out because the compound exhibits NH_2 resonance at δ 2-4.[12] In the solid state, infrared spectra of complexes 1a-1c show sharp N-H stretch bands in the 3300-3450 cm^{-1} region. Characteristic infrared stretching absorption of N-H stretch mode was observed at 3386 and 3364 cm^{-1} for 1a. The value is comparable to that of $Ru\{C_6H_4(NH)_2\text{-}1,2\}(PPh_3)_3$[13] appeared at 3360 cm^{-1}, that of $Cp^*Ir\{C_6H_4(NH)_2\text{-}1,2\}$ appeared at 3308 $^{-1}$, and those of bis(cyclopentadienyliron)arene complexes[18] with amine bridges appeared at 3500 and 3400 cm^{-1}. The mass spectrum of 1a gave the molecular ion of 230. The photochemical excitation (λ>250 nm) of compound 1a in the presence of unsaturated organic compound such as cyclohexene was inert. The reaction of Jonas reagent with diaminomaleonitrile gave a red solution according to Eq. 2.

(2)

ld
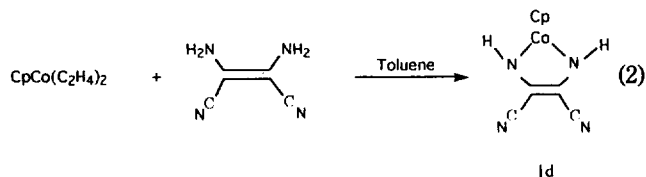
The ^{1}H NMR spectrum of 1d contained one signal of relative area 5 at δ 3.88, assigned to Cp together with a broad peak of relative area 2 at δ 8.38, assigned to NH protons, Infrared stretching absorption bands of v (NH) was observed at 3494 and 3351 cm^{-1}, together with peak of v (CN) at 2204 cm^{-1}. Although the complexes 1a-1d were confirmed by spectroscopic studies, the next question arises as to which mechanistic pathways led to the final product. The first plausible step would be the attack of one amine to cobalt fragment concomitant with extrusion of one ethylene, leading to N-H bond activation (chart 1) followed by the insertion reaction, although evidence is lacking.


3   1a
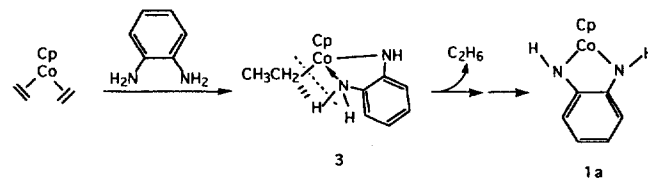
Another amine in 3 would be coordinated to cobalt. The final step probably proceeds with a four-centered mechanism to form a cobalt diamido complex, as in the case of C-H bond activation.[19]

Electronic Absorption Spectra. The cobalt complex 1a (see Table 1) shows two energy maximum at 258 and

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Table 1. Electronic Absorption Spectra of Complexes **1a-1d**

Complex	Solvent	λ_{max}, nm	ε, $M^{-1}cm^{-1}$
1a	CH_2Cl_2	258	28000
		432	19000
1b	CH_2Cl_2	254	23000
		422	17000
1c	CH_2Cl_2	250	24000
		418	19500
1d	CH_2Cl_2	255	22000
		414	4200
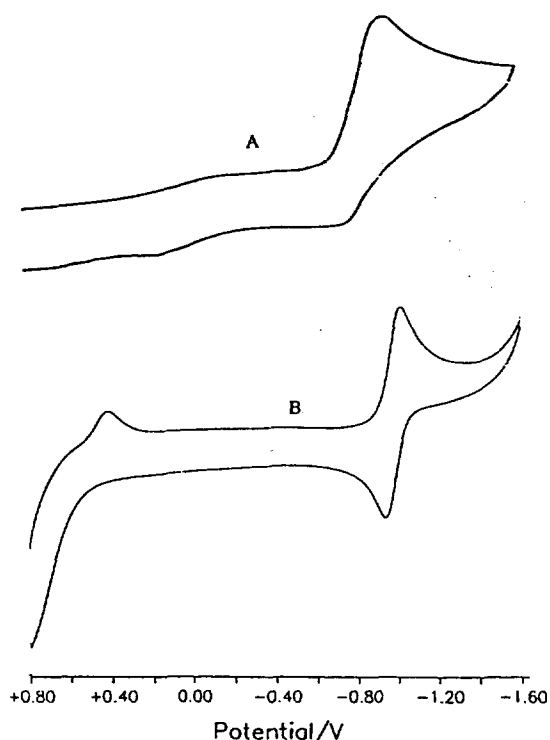
Figure 1. (A) Cyclic voltammogram of **1a** in 0.1 M (n-Bu$_4$N)(ClO$_4$)-DMF electrolyte solution. (B) Cyclic voltammogram of **1d** in 0.1 M (n-Bu$_4$N)(ClO$_4$)-DMF electrolyte solution.

432 nm, which are assigned to a combination of a metallacycle $\pi{\rightarrow}\pi^*$ transition and a $d{\rightarrow}\pi^*$ transition. These assignments resemble those proposed for CpCo(1,4-H$_2$H$_4$)[20] and Cp*Ir {C$_6$H$_4$(NH)$_2$-1,2}.[15] The extinction coefficients (28000, 19000 $M^{-1}cm^{-1}$) of **1a** tell us that these transitions are charge-transfer bands.

Electrochemistry. Complex **1d** displays a quasi reversible reduction in the cyclic voltammogram at a potential of −1.14 V vs an Ag/AgCl reference. The cyclic voltammogram of **1d** is shown in Figure 1. However, the cyclic voltammogram of **1a** showed that the complex was reduced at −0.97 V. It may be attributable to the difference of a delocalization in the metallacycle. The reduction pattern is quite similar to that of Cp*Ir{C$_6$H$_4$(NH)$_2$-1,2}.[15]

Experimental Section

All manipulations of air-sensitive materials were carried out under an argon atmosphere with use of standard Schlenk or vacuum line technique or a Mebraun MB150 glovebox. ^{1}H NMR spectra were recorded on a Bruker WM-250 spectrometer in C$_6$D$_6$. Chemical shifts are given in parts per million relative to TMS for ^{1}H NMR spectra. IR spectra were obtained by using a Perkin-Elmer 1310 instrument. Mass spectra were measured on a high resolution VG70-VSEG spectrometry. Cyclic voltammetry was carried out with a Potentiostat-Galvanostat Model 273 at a glassy-carbon electrode with an Ag/AgCl couple as a reference and tetra-n-butyl ammonium perchlorate (TBAP) as an electrolyte in CH$_3$CN. Reagent grade toluene and hexane were distilled under argon sodium-benzophenone ketyl. CpCo(C$_2$H$_4$)$_2$ were prepared according to literature methods.[1] C$_6$H$_4$(NH$_2$)$_2$-1,2, NC(NH$_2$)C =C(NH$_2$)CN, 4,5-(CH$_3$)$_2$-C$_6$H$_4$(NH$_2$)$_2$-1,2,4,5-(Cl)$_2$-C$_6$H$_2$(NH$_2$)$_2$-1, 2 were purchased from Aldrich.

Preparation of CpCo{C$_6$H$_4$(NH)$_2$-1,2} (1a). To a stirred toluene solution (20 ml) of CpCo(C$_2$H$_4$)$_2$ (0.4 g, 2 mmol) saturated with C$_2$H$_4$ was added C$_6$H$_4$(NH$_2$)$_2$-1,2 (0.24 g, 2 mmol) in the toluene (10 ml) dropwise. The solution was stirred at room temperature for 72 hr. The volume was reduced to ca. 5 ml and chromatographed on neutral silicagel with use of hexane (90%)/toluene (10%) mixture as eluent under argon. The second red band was collected and the volume was reduced to ca. 20 ml. The red crystals were obtained by leaving the solution in a refrigerator at −78 ℃. The yield was 72%. mp. 163 ℃. ^{1}H NMR (C$_6$D$_6$) δ 8.96 (br, 2H, NH), 7.06 (m, 2H, aromatic), 6.53 (m, 2H, aromatic), 4.53 (s, 5H, Cp); IR (on KBr pellet; cm^{-1}) 3386 (m), 3364 (m), 3290 (br), 3184 (br), 3010 (m), 1633 (m), 1593 (m), 1502 (s), 1459 (m), 1275 (s), 1132 (w), 1050 (w), 1032 (w), 928 (w), 808 (m), 749 (s); mass spectrum, m/e (relative intensity) 230 (M$^+$, 32). Anal. Calcd. for C$_{11}$CoH$_{11}$N$_2$: C, 57.40; H, 4.80. Found : C, 56.94; H, 4.71.

Preparation of CpCo{4,5-(CH$_3$)$_2$-C$_6$H$_2$(NH)$_2$-1,2} (1b). The same procedure was taken as described in the preparation of **1a**. The yield was 48%. mp. 125 ℃. ^{1}H NMR (C$_6$D$_6$) δ 8.64 (br, 2H, NH), 6.84 (s, 2H), 4.42 (s, 5H, Cp), 1.21 (s, 6H, CH$_3$); IR (on KBr pellet;cm^{-1}) 3425 (m), 3208 (m), 2932 (m), 1682 (m), 1662 (m), 1602 (m), 1542 (m), 1414 (m), 1268 (m), 1108 (m), 1023 (m), 873 (w), 806 (s), 694 (w), 588 (w); mass spectrum, m/e (relative intensity) 258 (M$^+$, 52). Anal. Calcd for C$_{13}$CoH$_{15}$N$_2$: C, 60.50 : H, 5.80. Found : C, 60.12; H, 5.63.

Preparation of CpCo{4,5-Cl$_2$-C$_6$H$_2$(NH)$_2$-1,2} (1c). The same procedure was taken as described in the preparation of **1a**. The yield was 58%. mp. 143 ℃. ^{1}H NMR (C$_6$D$_6$) δ 9.21 (br, 2H, NH), 7.19 (s, 2H, aromatic), 4.98 (s, 5H, Cp) : Ir (on KBr pellet; cm^{-1}) 3425 (m), 3068 (m), 1664 (m), 1626 (w), 1502 (sh), 1464 (m), 1414 (s), 1364 (sh), 1236 (w), 1206 (w), 1084 (w), 1032 (w), 988 (m), 844 (m), 808 (m), 692 (br), 460 (m); mass spectrum, m/e (relative intensity) 299 (M$^+$, 38). Anal. Calcd. for C$_{11}$Cl$_2$CoH$_9$N$_2$: C, 44.20; H, 3.00. Found : C, 43.82; H, 2.83.

Preparation of CpCo{NC(NH)C=C(NH)CN-1,2} (1d). The same procedure was taken as described in the preparation of **1a** except that the solvent was stripped off and the compound was chromatographed on neutral silicagel with use of CH$_2$Cl$_2$ as eluent under argon. The yield was 62%. mp. 217 ℃. ^{1}H NMR (C$_6$D$_6$) δ 8.38 (br, 2H, NH), 3.88 (s, 5H, Cp); ^{13}C NMR (C$_6$D$_6$) δ 120.47 (CN), 90.65 (C=C), 76.18 (C$_5$H

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₅); Ir (on KBr pellet; cm⁻¹) 3494 (w), 3351 (m), 3283 (m), 2204 (s), 1643 (br), 1392 (w), 1366 (br), 1340 (w), 1262 (w), 1108 (br), 1054 (br), 808 (w), 716 (w), 516 (w); mass spectrum, m/e (relative intensity) 230 (M^+, 48). Anal. Calcd. for $C_9CoH_7N_4$: C, 47.00; H, 3.00. Found : C, 46.48; H, 2.82.

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19. (a) Hackett, M.; Ibers, J. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1436. (b) Saillard, J.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006.
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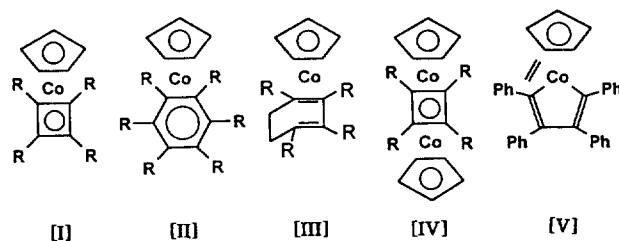# Reaction of CpCo(C₂H₄)₂ with Diphenylacetylene

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Since the first preparation of π-complexes of cyclobutadiene containing transition metals such as Ni, or Fe, the actual existence of cyclobutadiene fragment at room temperature has been reported.[1-2] 1,2,3,4-Tetraalkyl cyclobutadiene-cobalt complexes were prepared by the reaction of (η^5-cyclopentadienyl)di(carbonyl)cobalt[3] with dialkylacetylene in 1978.[4-5] Recently, (η^5-cyclopentadienyl)bis(ethylene)cobalt(Jonas reagent)[6] has been used for introducing (η^5-cyclopentadienyl)cobalt(CpCo)-moiety in the complex, CpCoL (L; 4π-electron donor ligand). Jonas reagent reacts with dialkylacetylene to give complexes [I], [II], [III] and [IV].[7]

[I]   [II]   [III]   [IV]   [V]

In this paper we would describe the reaction and coordination chemistry of Jonas reagent with diphenylacetylene. A new complex, (η^5-cyclopentadienyl)ethylene(2,3,4,5-tetraphenyl cobaltacyclo-2,4-pentadiene)[V] was obtained in 77.4 % yield as a single product.[8] It is suggested that two molecules of diphenylacetylene are attacking cobalt metal of Jonas reagent to replace one of the two ethylene molecule in the reagent leaving an intermediate which has one molecule of ethylene and two molecules of diphenylacetylene.[7] This intermediate is expected to be unstable because it has 20 valence electrons (VE). Further rearrangement by dimerization of two diphenylacetylene molecules gave more stable complex [V] with 18 VE. The NMR spectrum of complex[V] showed that δ-values of ethylene in Jonas reagent shifted from 2.38, and 0.59 ppm to 2.43, and 1.50 ppm respectively, and that was due to the ring current effect of neighboring phenyl ring. Among the protons of four phenyl groups attached in the complex[V], those of the phenyl ring near ethylene molecule showed at 7.38 ppm and the other protons of the remaining three phenyl rings appeared broadly at 7.08 ppm. Molecular ion peak of complex[V] in mass spectrum was observed at m/e 508, and m/e 480 peak resulted from the elimination of ethylene from the complex[V].

We also found that the complex[V] was further decomposed during the chromatographic separation. Dark red crystalline complex[V] was dissolved in petroleum ether and separated as two bands on a silicagel column (2×15 cm). The